Miscibility and Crystallization Behavior of Poly(ether ether ketone ketone)/Poly(ether imide) Blends

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ABSTRACT: The miscibility and crystallization behavior of poly(ether ether ketone ketone) (PEEKK)/poly(ether imide) (PEI) blends prepared by melt-mixing were investigated by differential scanning calorimetry. The blends showed a single glass transition temperature, which increased with increasing PEI content, indicating that PEEKK and PEI are completely miscible in the amorphous phase over the studied composition range (weight ratio: 90/10–60/40). The cold crystallization of PEEKK blended with PEI was retarded by the presence of PEI, as is apparent from the increase of the cold crystallization temperature and decrease of the normalized crystallinity for the samples anealed at 300°C with increasing PEI content. Although the depression of the apparent melting temperature of PEEKK blended with PEI was observed, there was no evidence of depression in the equilibrium melting temperature. The analysis of the isothermal crystallization at 313–321°C from the melt of PEEKK/PEI (100/0, 90/10, and 80/20) blends suggested that the retardation of crystallization of PEEKK is caused by the increase of the crystal surface free energy in addition to the decrease of the mobility by blending PEI with a high glass transition temperature. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 769–775, 2001

Key words: miscibility; crystallization behavior; melting behavior; poly(ether ether ketone ketone); poly(ether imide)

INTRODUCTION

Poly(aryl ether ketone)s (PAEKs) such as poly(ether ether ketone) (PEEK) and poly(ether ether ketone ketone) (PEEKK) are semicrystalline polymers having a high continuous-use temperature, excellent solvent resistance, and superior mechanical properties. However, the modulus of these materials decreases at elevated temperature because of a relatively low glass transition temperature (T_g) around 140–150°C. On the other hand, poly(ether imide) (PEI, Ultem of General Electric Co.) is an amorphous polymer with a high T_g of 215°C. However, PEI has a lower chemical resistance than that of PEEK and cannot be used above its T_g. Therefore, blending these two polymers seems an interesting route to combine the complementary properties of both polymers. Actually, since it was reported that PEEK and PEI are miscible over the whole composition range in the amorphous state and that the T_g of the blend increases with increasing PEI content,[1] PEEK/PEI blends have been the subject of several investigations.[2–6] In the present article, the miscibility and crystallization behavior of PEEKK/PEI blends prepared by melt-mixing were studied by differential scanning calorimetry (DSC). This article discusses the influence of PEI on the crystallization of PEEKK based on the analysis of the isothermal crystallization process.

EXPERIMENTAL

Materials

PEEKK, having the approximate number-average molecular weight (M_n) of 100,000, was kindly supplied by Professor Z. Wu of Jilin University of China. PEI was obtained from the General Electric Plastics Japan (Chuo-ku, Tokyo, GE, Ultem 1000). The number-average molecular weight (M_n) is 12,000, and the weight-average molecular weight (M_w), 30,000.

Sample Preparation

The polymers were dried at 130°C in a vacuum oven for at least 5 h before use. Blending of PEEKK and PEI was performed using a Labo-plasto-Mill with a twin rotary mixer (Toyo Seiki Co. Ltd., Japan). The molten mixing was carried out at 390°C, the rotary speed was 50 rpm, and the mixing time was 5 min. The weight ratios of PEEKK/PEI were 100/0, 90/10, 80/20, 70/30, 60/40, and 0/100. Amorphous films of PEEKK/PEI with a thickness of about 0.2 mm were prepared by compression molding of the pulverized power at 410°C for 10 min, followed by quenching in ice water. Posttreatments to the films included anealing the initial amorphous films at 300°C for 40 min, followed by cooling naturally to room temperature.

Measurements

Differential scanning calorimetry (DSC) was performed on a DSC-3100 instrument (MAC Science Co., Japan) for heating scans and on a Perkin–Elmer DSC Pyris 1 DSC for isothermal measurement. Heating scans of the amorphous films for determining the T_g, cold crystallization temperature (T_c'), and melting temperature (T_m) were carried out at a heating rate of 10°C/min in a nitrogen atmosphere. The samples for isothermal crystallization were heated to 420°C at a rate of 20°C/min, held at this temperature for 5 min, and then cooled to the appropriate crystallization temperature (T_c) at a rate of 200°C/min. The heat generated during the development of the crystalline phase was recorded until no further heat evolution was observed and analyzed according to the usual procedure in order to obtain the relative degree of crystallinity. The relative degree of crystallinity as a function of time was found from eq. (1):

$$\chi_c(t)/\chi_c(\infty) = \int_{t_0}^{t} (dH/dt) \, dt / \int_{t_0}^{\infty} (dH/dt) \, dt \quad (1)$$

Table I   Calorimetric Data for Amorphous PEEKK/PEI Blends on the First Heating Scan

PEEKK/PEI	T_g (°C)	T_c' (°C)	T_m (°C)
100/0	152.9	184.2	369.6
90/10	160.5	209.8	345.7
80/20	166.3	229.3	340.2
70/30	173.5	234.0	337.9
60/40	177.6	264.6	337.9
0/100	217.0	—	—

where t_0 is the time at which the sample attains isothermal conditions, as indicated by a flat baseline after the initial spike in the thermal curve; $\chi_c(t)$, the degree of crystallinity at time t; $\chi_c(\infty)$, the ultimate crystallinity at a very long time; and dH/dt, the heat-flow rate. At the end of each isothermal experiment, the samples were reheated at a heating rate of 10°C/min for measuring the melting temperature.

RESULTS AND DISCUSSION

Miscibility and Thermal Properties of PEEKK/PEI Blends

Thermal transitions of PEEKK, PEI, and PEEKK/PEI blends were evaluated from the first heating DSC scans of the amorphous films. The T_g, T_c', and T_m values obtained for quenched PEEKK are 153, 184, and 370°C, respectively (Table I). On the other hand, the DSC thermogram of PEI showed only a T_g at 217°C. The amorphous PEEKK/PEI blends showed a single T_g, which value increased with increasing content of PEI. Figure 1 shows plots of T_g versus PEI content. The solid line represents the Fox equation:

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \quad (2)$$

where w_1 and w_2 represent the weight fractions of the blend constituents, and T_{g1} and T_{g2}, their respective glass transition temperatures. The T_g of the blend approximately obeyed the Fox equation within experimental error. These results indicate that PEEKK and PEI are miscible in the amorphous state at the studied composition range.

On the heating scan of all the amorphous samples, the T_c' caused by the crystallization of the PEEKK component from the miscible amorphous
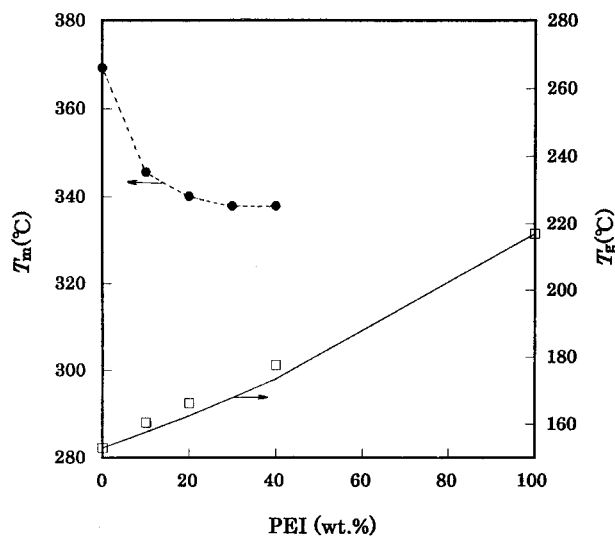
Figure 1 Glass transition temperature and melting temperature on the first heating scan of the DSC measurement versus PEI content for amorphous PEEKK/PEI blends. ($\square$) T_g and ($\bullet$) T_m are the experimental data and the solid line indicates the calculated T_g values according to the Fox equation.

phase of PEEKK and PEI was observed. The T_c' increased with increasing PEI content, suggesting that the mobility of a crystallizable segment is decreased by the incorporation of PEI with a high T_g. Also, on the heating scan, a broad single melting temperature was observed, which was depressed by the PEI content. However, such a depression does not truly reflect the equilibrium melting behavior, since the degree of crystallinity and the crystallization rate are different in these samples. The equilibrium melting point of the blends is discussed in the following section.

In Figure 2, the DSC thermograms of PEEKK/PEI (100/0–60/40) samples anealed at 300°C for 40 min show the double-melting behavior. Wu et al. also reported a double-melting behavior for the PEEKK sample annealed at 225–300°C.[7] They concluded from the study on the influence of thermal treatment that the higher melting crystallites are formed prior to the formation of the lower melting ones. They also described that the lower melting crystallites reorganize to some extent during the DSC scan and eventually can become a part of the higher melting crystallites at higher temperature. A similar effect was found in the melting behavior of PEEK.[8–10] In our blend system, PEEKK/PEI (70/30 and 60/40) samples annealed at 300°C for 40 min showed a broad exothermic peak (310–320°C) which is not observed

for pure PEEKK system, in addition to a broad melting peak (330–345°C). It is thought that the occurrence of the exotherm for the PEEKK/PEI blends with higher PEI content relates to the reorganization of crystals during DSC scan and that reorganization of crystals during the isothermal annealing at 300°C for 40 min before the DSC measurement is hindered by the presence of PEI. Such an exothermic behavior was also reported for PEEK/PEI blends by Crevecoeur and Groeninckx.[2] The lower melting peak (T_{m1}) for the PEEKK/PEI (70/30 and 60/40) blends could not be determined because of the appearance of a recrystallization exotherm. The degree of crystallinity (χ_c) and its normalized value ($\chi_{c(\text{PEEKK})}$) by the PEEKK weight fraction (w_{PEEKK}) in the blend can be estimated from the DSC results by using the following equations:
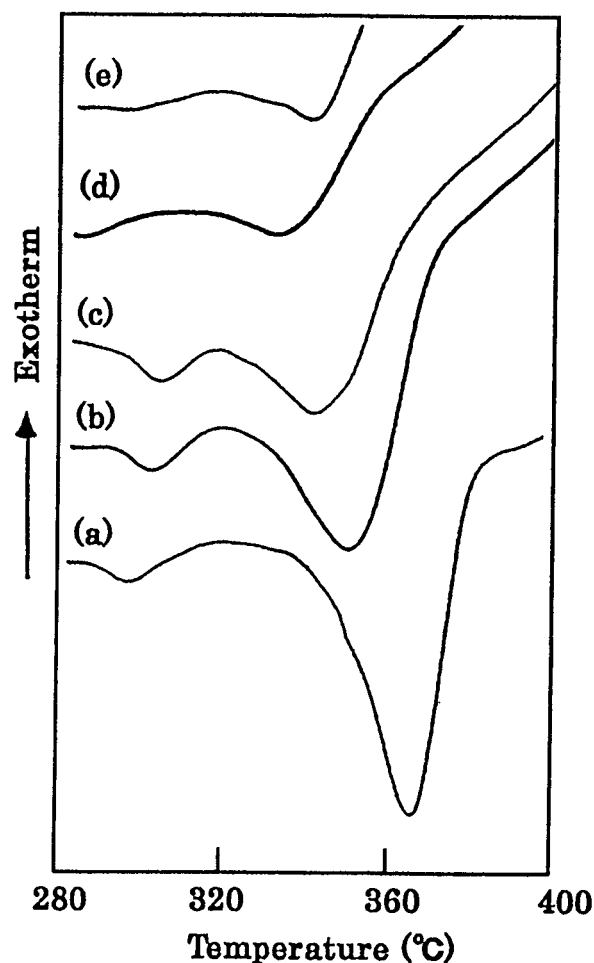

Figure 2 DSC thermograms of PEEKK/PEI, (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30, and (e) 60/40, blends annealed at 300°C for 40 min.

Table II   Melting Temperature and Crystallinity for the PEEKK/PEI Blends Annealed at 300°C for 40 Min

PEEKK/PEI Weight Ratio	T_{m1} (°C)	T_{m2} (°C)	χ_c (wt %)	$\chi_{c(\text{PEEKK})}$ (wt %)
100/0	300.0	365.0	18.47	18.47
90/10	304.3	348.6	14.96	16.62
80/20	305.9	340.1	11.82	14.78
70/30	—	331.6	9.05	12.93
60/40	—	338.6	6.65	11.08

$$\chi_c = \Delta H/\Delta H_m^0 \qquad (3)$$

$$\chi_{c(\text{PEEKK})} = \chi_c/w_{\text{PEEKK}} \qquad (4)$$

where ΔH is the heat of fusion based on the higher melting point (T_{m2}) of the blend determined by DSC and ΔH_m^0 is the heat of fusion of 100% crystalline PEEKK ($\Delta H_m^0 = 124$ J/g).[11] The crystallinity data are given in Table II. Both the χ_c and $\chi_{c(\text{PEEKK})}$ values decreased with increasing PEI content, in agreement with the hinderance of crystallization by the presence of PEI.

Isothermal Crystallization Kinetics of PEEKK/PEI Blends

The isothermal crystallization kinetics of PEEKK/PEI (100/0–80/20) blends over a temperature range of 313–321°C were analyzed using the Avrami equation:

$$\chi_c(t)/\chi_c(\infty) = 1 - \exp(-kt^n) \qquad (5)$$

where k is the rate constant of crystallization and n is the Avrami exponent, which can be related to the type of nucleation and to the geometry of crystal growth. The analysis of PEEKK/PEI blends with the PEI content over 30 wt % at the same crystallization temperature region was difficult because of the very low crystallization. From the intercepts and the slopes of the plots of $\log\{-\ln[1 - \chi_c(t)/\chi_c(\infty)]\}$ versus $\log t$ (example plots for PEEKK/PEI 90/10, Fig. 3), the values of k and n were calculated, respectively; all these values are summarized in Table III. Each curve has a linear portion followed by a gentle roll-off at longer times. The values of the Avrami exponent n of the PEEKK/PEI blends are about 2 for both pure PEEKK and PEEKK/PEI blends, almost independent of the crystallization temperature and

composition. The exponent $n = 2$ obtained for PEEKK is consistent with the value reported by Wu et al.[7] These results suggest that the PEEKK/PEI blends have the same nucleation mechanism and the form of crystal growth as that of pure PEEKK. The crystallization half-times, $t_{1/2}$, the time at which the relative degree of crystallization is 0.5, increase with increasing crystallization temperature and PEI content. The rate constant k values decrease with increasing crystallization temperature and PEI content.

According to the Hoffman–Weeks theory,[12] the dependence of the apparent melting temperature T_m on the crystallization temperature (T_c) is given by

$$T_m = (1 - 1/\gamma)T_m^0 + (1/\gamma)T_c \qquad (6)$$

where T_m^0 is the equilibium melting point and γ is the lamellar thickening factor which describes the growth of lamellar thickness during crystallization. Equation (6) shows that T_m^0 and γ can be determined from the intersection with the $T_m = T_c$ line and the slope, respectively, in a Hoffman–Weeks plot of T_m versus T_c. The higher melting temperature (T_{m2}) of double melting peaks observed at the heating scan after isothermal crystallization was plotted against T_c for PEEKK and PEEKK/PEI (90/10 and 80/20)
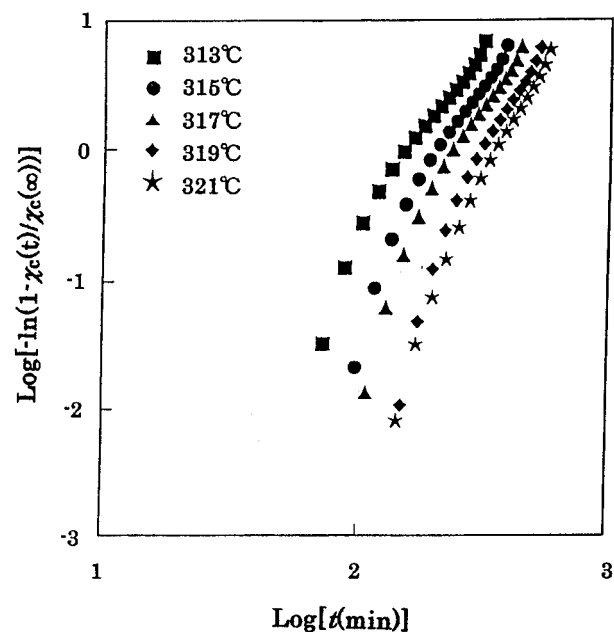

Figure 3   Example plots of $\log\{-\ln[1 - \chi_c(t)/\chi_c(\infty)]\}$ versus $\log t$ for PEEKK/PEI (90/10) blend.

Table III Isothermal Crystallization Parameters for PEEKK in the Blends with PEI

PEEKK/PEI	T_c (°C)	n	k (min^{-n})	t_{max} (s)	$t_{1/2}$ (s)
100/0	313	2.1	1.26×10^{-4}	69.5	88.3
	315	2.1	3.52×10^{-5}	77.2	97.2
	317	2.2	1.03×10^{-5}	89.5	110.6
	319	2.2	8.14×10^{-6}	98.1	121.5
	321	2.3	1.13×10^{-6}	107.4	132.4
90/10	313	2.0	3.95×10^{-5}	111.0	132.5
	315	2.0	2.19×10^{-5}	153.0	178.1
	317	2.2	3.22×10^{-6}	180.0	209.1
	319	2.3	5.03×10^{-7}	246.0	277.2
	321	2.3	1.80×10^{-7}	298.2	316.3
80/20	313	2.0	1.05×10^{-5}	261.1	282.3
	315	2.1	4.56×10^{-6}	278.3	301.4
	317	2.1	1.01×10^{-6}	310.8	335.2
	319	2.2	2.05×10^{-7}	343.5	371.4
	321	2.3	3.63×10^{-8}	394.2	423.1

blends (Fig. 4). The slope of the plots changed around 322°C for PEEKK/PEI 90/10 and 80/20 blends. A similar change of slope is also observed for PEEK/PEI blends.[4] In such a case, the melting temperature observed at a higher crystallization temperature should be adopted, because the formed crystals are expected to have fewer defects. Therefore, when the plots above 322°C were extraporated, a T_m^0 of about 387°C was obtained for all the samples, which value is close to the literature values of PEEKK at 385 and 387°C reported by Zimmermann and Könnecke[11] and Wu et al.,[7] respectively. The obtained T_m^0 was little affected by the presence of PEI. A similar result was also reported by Hsiao and Sauer for PEEK/PEI blends.[4] However, Lee et al. reported that T_m^0 decreased with increasing content of PEI for a nylon-6/PEI blend.[13] In this case, T_{m1} (lower melting point) was adopted as a T_m. For the polymer showing double-melting behavior, this often gives rise to controversies with respect to which is the most appropriate melting point. In our blend system, when the plots of T_{m1} were extrapolated, extraordinaly high values over 400°C were obtained. Therefore, the T_m^0 based on the values of T_{m2} was used for the following determination of the surface free energy using the Lauritzen–Hoffman equation.[14]

Theories of surface nucleation have been modified to account for the effects of the non-crystallizable component on the linear growth rate of crystals developing in undercooled homogeneous blends.[15–18] At present, because of lack of information on diffusion constants in polymer blends, the equation commonly used to describe the linear growth kinetics is[13,19]

$$G = \varphi_2 G_0 \exp\{-U/[R(C_2 + T_c - T_g(\varphi)]\}$$
$$\times \exp\{-rb_0\sigma\sigma_e T_m^0(\varphi)/[k_B f\Delta H_m^0 T\Delta T(\varphi)]\}$$
$$\times \exp\{2\sigma T_m^0(\varphi)\ln \varphi_2/[b_0 f\Delta H_m^0 \Delta T(\varphi)]\} \quad (7)$$

where φ_2 is the volume fraction of a crystallizable polymer; U, the activation energy for transport of crystallizable segments to the crystal front through the undercooled melt; $T_g(\varphi)$, the T_g of the blend; $T_m^0(\varphi)$, the equilibrium melting temperature of the PEEKK blended with PEI ($T_m^0 = 387 + 273 = 660$ K) in this case; k_B, the Boltzmann constant; C_2, a constant usually assumed to be 51.6°C; f, a correction factor for the temperature dependence of the heat of fusion and can be expressed as $f = 2T_c/[T_m^0(\varphi) + T_c]$; σ and σ_e, the lateral and fold surface free energies of the developing crystals, respectively; and b_0, the layer thickness. G_0 is a constant that depends on the regime of crystallization, and r is a parameter characteristic of the growth regime: $r = 4$ in Regimes I and III and $r = 2$ in Regime II. $\Delta T(\varphi)$ is the degree of undercooling [$\Delta T(\varphi) = T_m^0(\varphi)$
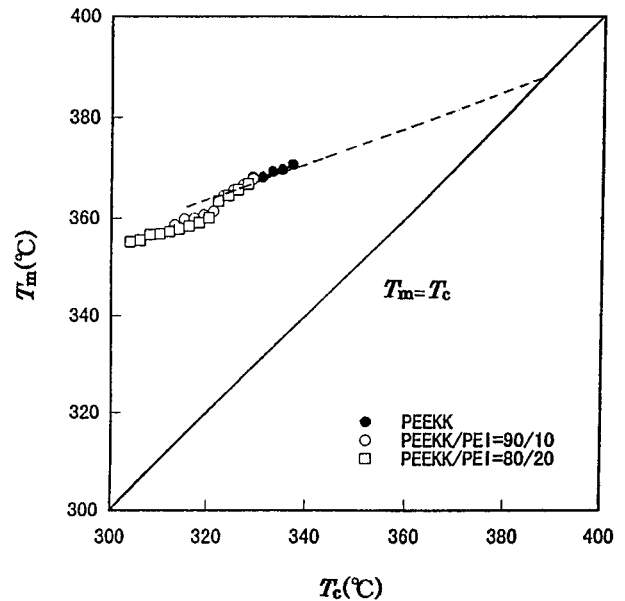

Figure 4 Hoffman–Weeks plots to determine the equilibrium melting temperature of PEEKK with different PEI compositions.

$-T_c$] experienced by the crystallizable chain in the blend. From eq. (7), two main factors can be taken into account to explain the retardation of crystallization of PEEKK blended with PEI: The dilute effect related to φ_2 diminishes the number of crystallizable chains at the growing lamella front; the increment of $T_g(\varphi)$ associated with the presence of mixed PEI with a high T_g in the PEEKK phase decreases the mobility of a crystallizable segment.

In addition to these two factors, the following analysis was performed to evaluate the contribution of the crystallization surface free energy. The relationship to the linear growth rate (G) and Avrami parameter k can be written as

$$G \propto k^{1/n} \tag{8}$$

Combining eqs. (7) and (8), followed by rearrangement, gives eq. (9):

$$\alpha = (\ln k)/n + U/\{R[C_2 + T_c - T_g(\varphi)]\}$$
$$- \{1 + 2\sigma T_m^0(\varphi)/[b_0 f \Delta H_m^0 \Delta T(\varphi)]\}\ln \varphi_2$$
$$= \ln G_0 - rb_0 \sigma \sigma_e T_m^0(\varphi)/[k_B f \Delta H_m^0 T \Delta T(\varphi)]$$
$$= \ln G_0 - K_g T_m^0(\varphi)/[fT\Delta T(\varphi)] \tag{9}$$

where the kinetic parameter K_g is equal to $rb_0 \sigma \sigma_e/(k_B \Delta H_m^0)$. Therefore, by plotting α as a function of $1/[fT\Delta T(\varphi)]$, straight lines with slopes related to the surface free energies of the lamellar crystals should be obtained.

The present data obtained from the PEEKK/PEI (100/0, 90/10, and 80/20) blend are plotted in Figure 5 according to eq. (9). The n and k values were evaluated from the preceding Avrami analysis. The values of U = 8.38 kJ/mol and C_2 = 51.6°C were taken from the literature on the crystallization kinetics of pure PEEK.[9,20] The adoption of the same values had been done for the crystallization kinetics studies of pure PEEKK.[7] It should be noted that alternative reasonable choices of these values do not significantly affect the slopes of the lines in Figure 5, as can be expected for crystallizations at temperatures well above the T_g. The values of b_0 = 0.489 nm and σ = 9 erg cm^{-2} were taken from the literature.[21] Figure 5 shows that the experimental data approximately obey eq. (9), although some deviation from the straight line was observed, especially in the pure PEEKK. The kinetic parameter K_g calculated from the slope is evaluated to be 994, 1109, and 1163 K for the PEEKK/
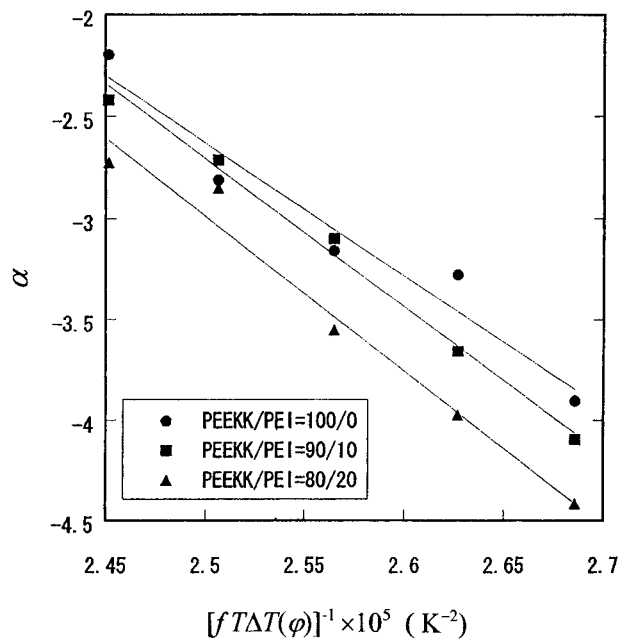

Figure 5   Plots of kinetic data according to eq. (9) for PEEKK/PEI blends.

PEI (100/0, 90/10, and 80/20) blends, respectively. Although the obtained value of K_g for pure PEEKK is slightly higher than that reported by Wu et al.[7] (851.1 K), the difference may be allowable, considering the accuracy of the slope. The PEEKK/PEI (90/10 and 80/20) blends have a higher K_g than that of pure PEEKK, indicating that the product of the lateral and fold surface free energies $(\sigma\sigma_e)$ of the blend is higher than that of pure PEEKK. This may be causing the retardation of the crystallization of PEEKK blended with PEI, in addition to the decrease of mobility by the increase of the glass transition temperature.

CONCLUSIONS

PEEKK was miscible with PEI in the amorphous state over the studied composition range, as is revealed by the appearance of a single glass transition temperature which approximately obeys the Fox equation. For both cold- and melt-crystallization processes of PEEKK blended with PEI, the crystallization of PEEKK was retarded by the presence of PEI. Although the depression of the apparent melting temperature of PEEKK blended with PEI was observed, there was no evidence of depression in the equilibrium melting tempera-

ture. The analysis of the isothermal crystallization from the melt of PEEKK/PEI blends with PEI content not more than 20 wt % suggested that the retardation of the crystallization of PEEKK is caused by the increase of the crystal surface free energy in addition to the decrease of the mobility by blending PEI with a high glass transition temperature.

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